

Two-dimensional electron gas generation at the surface of the charge ordered BaBiO₃ semiconductor: a new physical mechanism

Verónica Vildosola,¹ Francisco Güller,^{1,2} and Ana María Llois^{1,2}

¹*Departamento de Materia Condensada, GIIA, CNEA-CONICET,
(1650) San Martín, Provincia de Buenos Aires, Argentina*

²*Departamento de Física, Universidad de Buenos Aires,
Ciudad Universitaria Pabellón I, (1428) Buenos Aires, Argentina*

In this work, we find by means of first principle calculations a new physical mechanism to generate a two-dimensional electron gas, namely, the breaking of charge ordering at the surface of a charge ordered semiconductor due to the incomplete oxygen environment of the surface ions. The emergence of the 2D gas is independent of the presence of oxygen vacancies or polar discontinuities; this is a self-doping effect. This mechanism might apply to many charge ordered systems, in particular, we study the case of BaBiO₃(001). In bulk, this material is a prototype of a forbidden valence compound in which the formal "metallic" Bi⁴⁺ is skipped exhibiting a charge disproportionated Bi³⁺-Bi⁵⁺ ordered structure. At room temperature, this charge disproportionation together with the breathing distortions gives rise to a Peierls semiconductor with monoclinic crystal structure. At higher temperatures ($T > 750\text{K}$) or upon doping, it turns cubic and metallic. Interestingly, doped BaBiO₃ was one of the first non-cuprates high- T_c superconductors discovered. The outer layer of the Bi-terminated simulated surface turns more cubic-like and metallic while the inner layers remain in the insulating monoclinic state. On the other hand, the metallization does not occur for the Ba termination, a fact that makes this system appealing for nanostructuring. Finally, this finding sets another possible route for future exploration: the potential scenario of 2D superconductivity at the BaBiO₃ surface.

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The emergence of high mobility two-dimensional electron gases (2DEGs) at the interfaces of insulating oxides has become a very exciting field of investigation[1] in the last decade. The realization of 2DEGs at the oxide interfaces brings about a wide variety of phenomena (superconductivity[2], magnetic-order[3], electron correlation-driven effects[4]) that have awakened the interest on both fundamental issues and their future technological applications.

It is nowadays an issue of intense debate what is the origin of the 2DEG at the oxide interfaces. One point of view ascribes it to polar/non polar interfaces and is based on the polar "catastrophe" model that proposes an electronic reconstruction to compensate the growing dipole moment as the number of polar layers increases. Another invoked mechanism is the presence of oxygen vacancies in the substrate. Each scenario explains part of the story[1, 5–7] and, probably, a complete understanding of the intrinsic nature of the 2DEG formation is highly dependent on the materials involved and the experimental set up. Recently, it has been shown that a 2DEG can also be generated in a simpler context, namely, at the vacuum-cleaved surface of SrTiO₃. In this case, a metallic gas is formed independently of the oxide bulk carrier densities, opening the way towards novel means of 2DEG generation at the surface of transition-metal oxides[8]. In this case, the presence of oxygen vacancies is suggested to lie behind the emergence of the metallic surface state.

In this work, based on Density Functional Theory(DFT)-calculations[9], we propose not only

a new candidate able to sustain a confined electron gas but also a new physical mechanism to generate it that is different from the ones invoked until now. We show, namely, that a 2DEG is formed at the (001) surface of insulating BaBiO₃ as a consequence of a charge order disruption. No external factors, such as polar discontinuities or oxygen vacancies are necessary to obtain, in this case, the 2DEG except for the Bi-terminated surface itself. The surface generated carrier densities are quite high and of the same order of magnitude as the ones measured at the sharp LaAlO₃/SrTiO₃ interfaces[1] or at the cleaved SrTiO₃ surfaces. This phenomenon might be present in many other charge ordered materials as will be discussed later.

In order to understand the nature of our finding we briefly describe the phase diagram of bulk BaBiO₃. At high temperature ($T > 750\text{K}$) it is a cubic perovskite exhibiting metallic behaviour. Formally, one would expect each bismuth to have a valence 4+. However, Bi is a typical valence-skipping atom, and even in the high temperature metallic phase, it presents charge disproportionation. At lower temperatures, this disproportionation couples to the tilting of the BiO₆ octahedra. The crystal structure goes through a rhombohedral phase ($750\text{K} > T > 405\text{K}$), becoming monoclinic for $T < 405\text{K}$ [10]. The charge disproportionation together with the structural distortion are further enhanced giving rise to a formal Bi⁵⁺-Bi³⁺ charge-ordered Peierls-like insulator in the low temperature monoclinic phase. The oxygen octahedra around the Bi ions present alternating

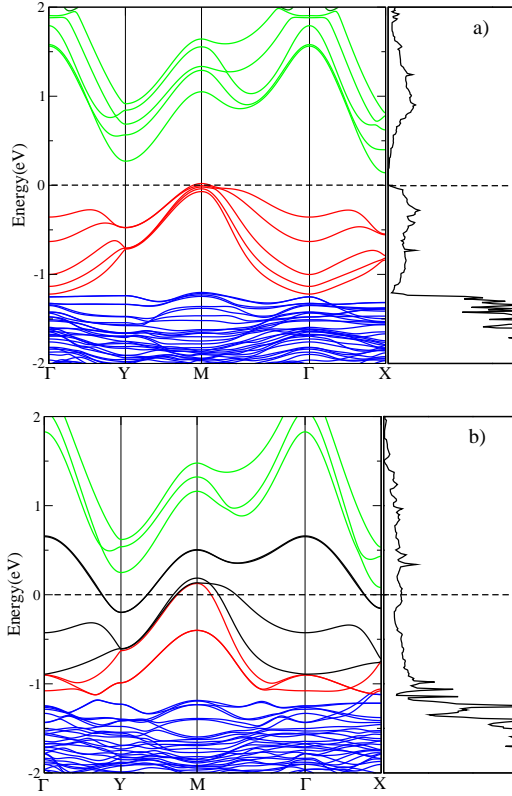


FIG. 1: (Color online) Bandstructure and total density of states for: a) Ba- terminated (11 layers) and b) Bi- terminated (9 layers) BaBiO_3 (001). The corresponding DOS plots are inverted (energy vs DOS) and the units are in eV.

breathing-in and breathing-out structural instabilities. Being the electronic properties of this material fascinating by themselves, the discovery of high- T_c superconductivity in doped BaBiO_3 [11, 12] made this system even more intriguing and interesting. It has been shown that upon doping, the monoclinic phase turns cubic or tetragonal (depending on the dopant) and metallic, exhibiting superconductivity with T_c 's as high as 30K.

Much of the understanding of the electronic structure and structural properties of both, the parent BaBiO_3 and the doped compounds, has been accomplished by means of first principle calculations[13–18]. In this material, the physics is dominated by spatially quite extended $\text{Bi}(s)\text{-O}(p)$ orbitals. In the absence of important correlation effects as in typical d or f electron systems, much progress has been made from early local-density approximation (LDA) calculations[19] based on DFT.

Calculations using LDA (or its gradient corrections GGA[20]) could explain the splitting of the $\text{Bi}(s)\text{-O}(p)$ band around E_F due to Peierls- like distortions that are switched on, in particular, by the breathing instability[18]. These calculations could account, then, for the charge disproportionation and its relation to the structural distortions in the monoclinic phase. LDA(GGA) results predict a pseudometallic behaviour,

however, it is well known that BaBiO_3 bulk presents an indirect gap whose experimental reported values go from 0.2 eV to 1.1 eV[21]. More recently it has been shown that in order to open the indirect gap and describe quantitatively the structural properties and the insulating behaviour of this phase of BaBiO_3 , it is necessary to go beyond standard DFT approaches, for instance by using hybrid functionals that combine a fraction of non-local exact exchange with local or semilocal approximations[22].

In this contribution, the theoretical study of the (001) surface of BaBiO_3 is faced for the first time. We perform first principles DFT calculations and take care of the gap problem by cross-checking the results with functionals that go beyond LDA or GGA. All the results presented in the main part of this work are done with a full-potential APW method in the GGA approximation as implemented in the Wien2k code[23]. In the Supplementary section we show that the main physical findings are confirmed using more sophisticated functionals. The surfaces are modeled by supercells with different slab thicknesses. We consider slabs composed by 9 to 15 layers that are stacked following the monoclinic crystal structure with both Ba- and Bi- terminated situations in the (001) direction. To avoid the interaction between opposite surfaces, they are separated in the z direction by an empty space volume ranging from 9 to 21\AA . The supercells have two inversion symmetric surfaces for simplicity. All internal atomic positions are allowed to relax.

Our calculations indicate that Bi- terminated BaBiO_3 turns metallic while the Ba-terminated case remains insulating as in the bulk (monoclinic phase). The results obtained for different supercells with different number of layers are qualitatively the same in the corresponding termination. The comparison among different slabs is useful to detect finite size effects (as described below).

In Fig. 1 we show the bandstructure and total densities of states (DOS) for a Ba- and a Bi- terminated slab, a) and b), respectively. It can be clearly seen that in the first case, the system behaves as an insulator while in the second one there are several bands crossing E_F , providing a considerably large amount of states visible in the corresponding DOS. These bandstructures correspond to slabs with 9 and 11 layers, having both of them ten Bi atoms in the slabs unit cell. In Fig. 1 a), the red bands have mainly $\text{Bi}^{3+}\text{-O}$ character and the green ones mainly $\text{Bi}^{5+}\text{-O}$ one. The blue bands have mostly O-p states with a significant Bi-6s weight. In Fig. 1 b), there are three green $\text{Bi}^{5+}\text{-O}$ bands above E_F and three red $\text{Bi}^{3+}\text{-O}$ bands below. One of the red bands crosses E_F , presenting a small pocket at the M point. This crossing is due to a finite size effect. The contribution of this pocket to the Fermi surface decreases with growing slab thickness. There are finally, four black interpenetrating bands that drive the system metallic. They basically come from the surface Bi atoms which are strongly mixed with O-p states.

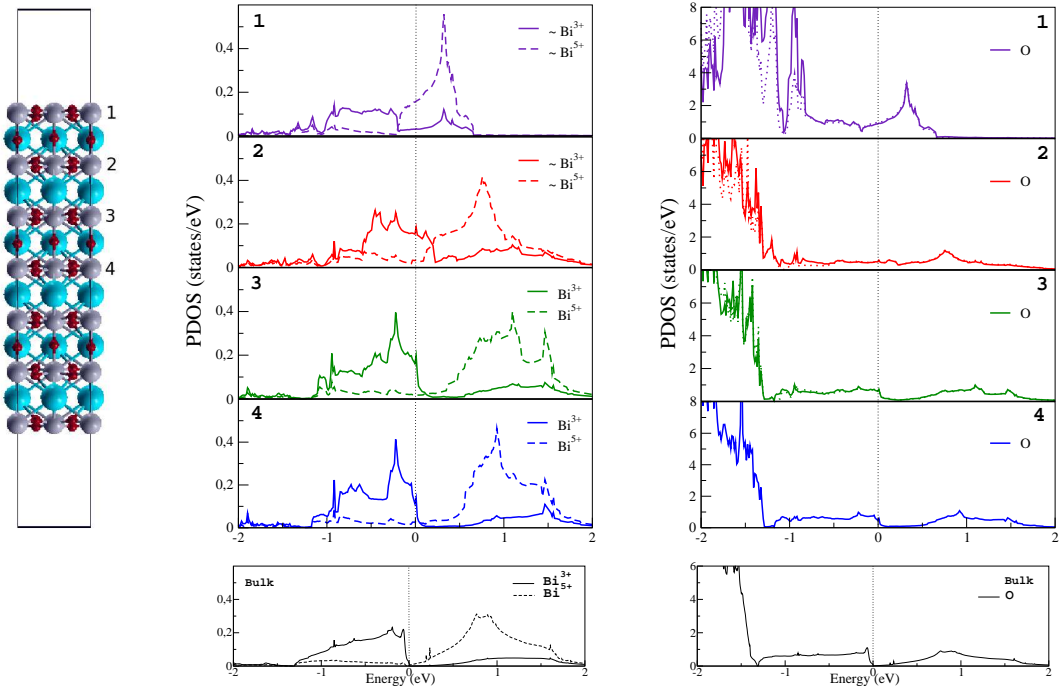


FIG. 2: (Color online) To the left, the simulated 13 layer slab with the BiO₂ planes labeled from 1 to 4. The projected DOSs on these planes are in the central and right plots, for the Bi-s and O projected states, respectively. The bottom row shows, for comparison, the corresponding DOSs for the bulk (monoclinic phase). E_F is at 0 eV.

The metallization of the Bi- terminated surface is a consequence of the incomplete octahedra environment of the Bi ions, which produces a rearrangement of the charge distribution suppressing the charge ordering at that BiO₂ plane. This suppression of the disproportionation is, in fact, partial but strong enough to turn the system metallic, as it is the case in the high temperature cubic phase of bulk BaBiO₃. On the other hand, for Ba surface termination, the oxygen octahedra environment of all Bi ions is complete, the charge ordering being then not affected in any of the BiO₂ planes. There is, indeed, a slight charge redistribution among the O atoms at the BaO surface plane, which has no effect on the insulating behavior of the whole system[24].

In order to trace the origin of this metallicity, in Fig. 2 we plot the DOSs projected onto the BiO₂ planes for the Bi- terminated 13 layer slab. The BaO layers are skipped for the sake of simplicity. The corresponding bulk projected DOSs are presented in the bottom row of Fig. 2, for comparison. The effects of charge disproportionation in the bulk can be clearly observed within the [-1.3 eV, 2 eV] energy range. There are quasi-symmetrically distributed occupied and empty 6s bands around E_F , presenting the Bi³⁺ ions mostly occupied states and the Bi⁵⁺ ions mostly empty ones. As mentioned before, there is an important Bi(6s)-O(p) hybridization, which is appreciable in the O projected DOS.

Our slab results show that already the third Bi layer from the surface, has a bulk like projected DOS. The

slight downward shift of the Fermi level for layers 3 and 4, as compared to the bulk, is again due to a finite size effect. The thinner the slab, the larger the downward shift of E_F into the 6s valence bands. The behaviour of the Bi-6s and O states of the surface and subsurface Bi-layers (labeled as 1 and 2) is qualitatively different to what happens in the deeper Bi planes. In layers 1 and 2 there is an effective charge transfer from the originally Bi³⁺ to the Bi⁵⁺ ion. The system turns, in this way, metallic and this metallicity is mainly confined to the two outer BiO₂ planes of the Bi- terminated BaBiO₃. For the thinner film considered, namely the 9 layer slab (not shown in Fig. 2), the confinement is less effective but still the metallization is predominantly at the outer layers.

The 2D carrier density, n_{2D} , is obtained from Luttinger's theorem as $n_{2D} \sim \frac{A_F}{2\pi^2}$, where A_F is the area enclosed by the 2D Fermi surface. The obtained n_{2D} for the Bi-terminated slabs is around 0.6 electrons per 2D unit cell (or $1.6 \times 10^{14} \text{ cm}^{-2}$). This carrier density is of the same order of magnitude as the ones estimated for sharp LaAlO₃/SrTiO₃ interfaces and cleaved SrTiO₃ surface[7, 8].

The charge redistribution at the Bi-terminated surfaces is present even in the unrelaxed systems, which turn metallic just by bond breaking. When the slabs are allowed to relax, the breathing distortions are washed out at the surface and subsurface Bi planes, contributing to an enhancement of the surface metallicity. In the deeper

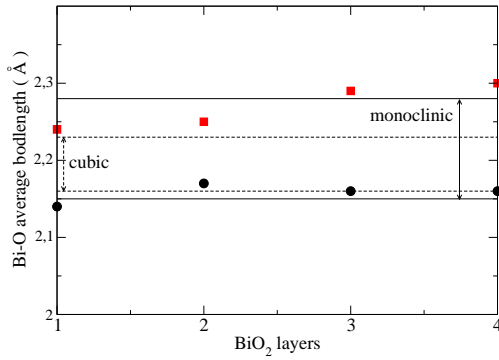


FIG. 3: (Color online) Averaged Bi-O bond lengths for the two types of Bi sites obtained for the 13 layer Bi-terminated BaBiO₃ slab. The label for each layer is the same as in Fig. 2. Squares(circles) correspond to the Bi³⁺-O(Bi⁵⁺-O) bond lengths, respectively. The solid and dashed straight lines are the corresponding values for low-T monoclinic and high-T cubic bulk phases, for comparison.

layers, compressed and expanded octahedra remain without significant changes preserving there the insulating charge ordering as in the bulk.

In Fig. 3 we plot the averaged Bi-O bond length of the Bi³⁺ and Bi⁵⁺ ions of each layer for the 13 layer slab. We observe that the structure turns cubic like as one approaches the surface. There is experimental evidence from thin films measurements supporting these results[25]. We can trace a parallelism between the effect of the surface on the structural and electronic properties of the Bi-terminated film and the effect of temperature on the same properties in bulk BaBiO₃. That is, we could think of having "cold" insulating monoclinic regions in the deeper planes and "hot" metallic cubic ones close to the surface.

We can also make an analogy with the high-T_c superconductor, the doped BaBiO₃ in bulk, which turns cubic and metallic upon doping with K or Pb. In this context, the predicted 2DEG at the BiO₂ surface deserves further investigation regarding its superconducting properties.

Another interesting finding with potential technological applications is the fact that the BaO surface is insulating. The possibility of *drawing* BiO₂ nanocircuits on top of BaO terminated BaBiO₃ surfaces constitutes a subject appealing for exploration.

Finally, this surface metallization phenomenon might be present in many other charge ordered materials. Potential candidates deserving further investigation are CaFeO₃[26], Pb₂O₃[27], LuNiO₃[28].

Summarizing, we predict the formation of a 2DEG at the Bi-terminated surface of BaBiO₃ (001). The physical mechanism behind the metallization of the surface is the breaking of charge order due to an incomplete oxygen octahedra environment of the Bi ions at the BiO₂ surface. The obtained metallic state is confined to the outer layers and presents a quite high 2D carrier density, of the

order of 0.6 electrons per 2D unit cell. This phenomenon is probably not exclusive of BaBiO₃ and might occur in other charge ordered semiconductors. It is independent of any external factor such as the ambient oxygen pressure or polar discontinuities, making out of this system a self-doping surface with promising potential applications to oxide electronics.

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- [1] A. Ohtomo and H. Y. Hwang, *Nature* **427**, 423 (2004).
 - [2] N. Reyren *et al*, *Science* **317**, 1196 (2007).
 - [3] A. Brinkman *et al.*, *Nature Materials* **6**, 493 (2007).
 - [4] R. Pentcheva and W. E. Pickett, *Phys. Rev. Lett.* **99**, 016802 (2007).
 - [5] A. Kalabukhov *et al.*, *Phys. Rev. B* **75**, 121404 (2007).
 - [6] G. Herranz *et al.*, *Phys. Rev. Lett.* **98**, 216803 (2007).
 - [7] M. Basletic and *et al.*, *Nature Materials* **7**, 621 (2008).
 - [8] A. F. Santander-Syro *et al.*, *Nature* **469**, 189 (2011).
 - [9] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
 - [10] D. Cox and A. Sleight, *Solid State Commun.* **19**, 969 (1976).
 - [11] A. W. Sleight *et al.*, *Solid State Commun.* **17**, 27 (1975).
 - [12] R. J. Cava *et al*, *Nature* **332**, 814 (1988).
 - [13] L. F. Mattheiss and D. R. Hamann, *Phys. Rev. B* **28**, 4227 (1983).
 - [14] L. F. Mattheiss and D. R. Hamann, *Phys. Rev. Lett.* **60**, 2681 (1988).
 - [15] A. I. Liechtenstein and *et al.*, *Phys. Rev. B* **44**, 5388 (1991).
 - [16] K. Kunc and *et al.*, *Solid State Commun.* **80**, 325 (1991).
 - [17] V. Meregalli and S. Y. Savrasov, *Phys. Rev. B* **57**, 14453 (1998).
 - [18] T. Thonhauser and K. M. Rabe, *Phys. Rev. B* **73**, 212106 (2006).
 - [19] J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
 - [20] J. P. Perdew *et al.*, *Phys. Rev. Lett.* **77**, 3865 (1996).
 - [21] See Ref. 22 and references there in.
 - [22] C. Franchini *et al.*, *Phys. Rev. B* **81**, 085213 (2010).
 - [23] P. Blaha *et al.*, *WIEN2k, An augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Techn. Univ. Wien, Austria, SBN 3-9501031-1-2., 2002).
 - [24] The obtained gap in the Ba-terminated films within GGA is a finite size effect. For sufficiently thicker slabs the bands coming from the inner layers should recover the pseudometallic behaviour obtained with GGA calculations for the bulk. We have checked that the gap gets considerably smaller for larger Ba-terminated supercells.
 - [25] H. Guyot, C. Filippini, and J. Marcus, *Journal of Alloys and Compounds* **195**, 543 (1993), ISSN 0925-8388.
 - [26] V. E. Alexandrov *et al*, *J. Chem. Phys.* **129**, 214704 (2008).
 - [27] W. A. Harrison, *Phys. Rev. B* **74**, 245128 (2006).
 - [28] I. I. Mazin *et al*, *Phys. Rev. Lett.* **98**, 176406 (2007).

I. SUPPLEMENTARY MATERIAL

Local or semilocal functionals of the exchange-correlation potential, such as LDA or GGA, predict a pseudometallic behavior instead of the well known semiconducting nature of the low temperature phase of bulk BaBiO_3 . In the main part of this contribution we predict, by means of DFT calculations using GGA, that a 2DEG is formed at the surface of a Bi-terminated $\text{BaBiO}_3(001)$ slab. We show there that the physical mechanism behind this metallization is a charge order breaking of the Bi ions at the surface. Although these GGA calculations are not able to reproduce the insulating nature of the core of a sufficiently thick slab, they can very well account for the charge ordering disruption. It has been recently shown that to better describe the insulating behavior of bulk BaBiO_3 it is necessary to go beyond standard LDA or GGA functionals, for instance by using hybrid functionals that combine a fraction of non-local exact exchange with local or semilocal approximations. [1, 2].

In the following we will show that the metallization of a Bi-terminated $\text{BaBiO}_3(001)$ slab is also obtained with more sophisticated functionals. We calculate the 9 layer slab using two other approaches, the Heyd-Scuseria-Ernzerhof hybrid functional (HSE)[3, 4] and the modified Becke-Johnson potential(mBJ) [5]. The HSE calculations are performed with the Vienna *ab initio* package (VASP) [6, 7], while the mBJ calculations are carried out with the Wien2k code [8]. The mBJ potential has been proposed by Tran and Blaha for a better description of band gaps. It is a local approximation to an atomic "exact-exchange"-potential and a screening term, plus the LDA correlation contribution. It has been shown that the mBJ potential provides a very good agreement with both the experimental data and the hybrid functionals or GW methods. The computational cost of the calculation using an mBJ potential is much less (by orders of magnitude) than the other two mentioned approaches, so that it can be applied to very large systems such as the ones we are interested here.

As far as we know, the mBJ potential has not been tested on bulk BaBiO_3 yet. In Fig. S1 we show the bandstructure and projected Bi-s DOS obtained by using (a) GGA, (b) mBJ, and (c) HSE.

The opening of an indirect gap can be clearly seen in the results using the mBJ and HSE functionals as compared to the pseudometallic behavior obtained with GGA. The

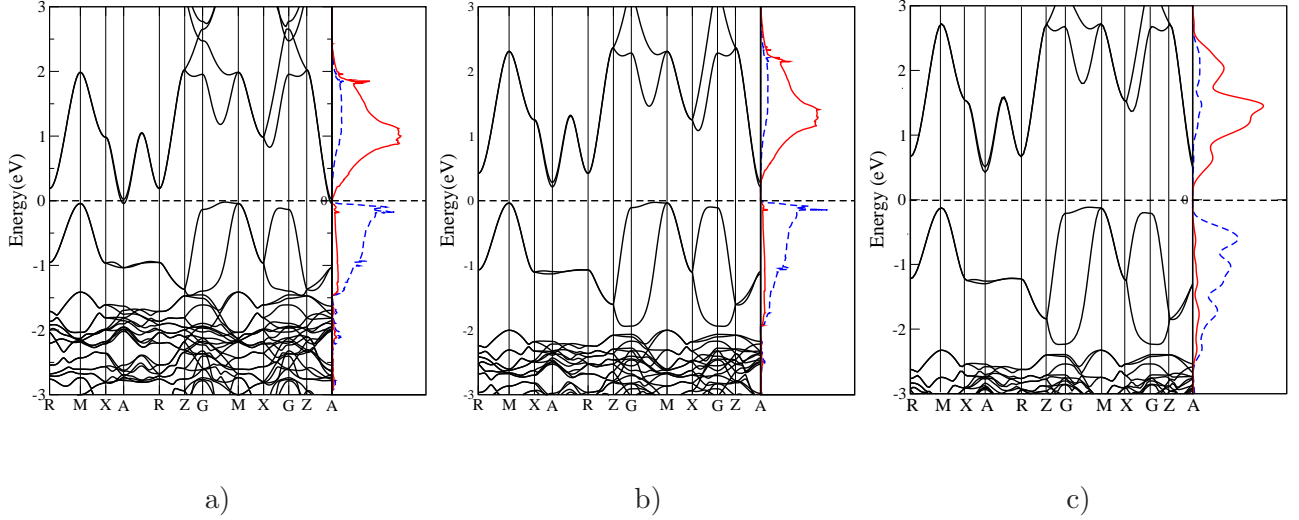


FIG. S1: (Color online) Bandstructure and corresponding Bi-s projected DOS for bulk BaBiO₃ using a) GGA, b) mBJ and c) HSE calculations. The DOS plots are inverted (energy vs DOS) and the units are in eV. The energy scale is similar to the one in Fig. 2.

experimental reported values for this gap go from 0.2 eV to 1.1 eV [2], so that both mBJ and HSE are well within this range. The position of the bands with mainly 2p character are also better reproduced with mBJ and HSE when compared with experimental photoemission spectra [9, 10]. Despite this gap problem, it can be noted in the corresponding projected Bi-s DOS, that the GGA results account reasonably well for Bi³⁺-Bi⁵⁺ charge disproportionation. This is the key ingredient for the main results of this contribution.

In Fig. S2, we present the total DOS obtained with GGA, mBJ and HSE for the 9 layer Bi-terminated slab. We can see that the main O-2p band moves to more negative energies following the sequence GGA-mBJ-HSE, similarly as in bulk BaBiO₃. Besides this difference, the metallization of the system in the three calculations is assertive.

In Fig. S3, we plot the bandstructure obtained using the mBJ potential. Around the Fermi energy, it looks very similar to the GGA one, presented in the Fig. 1b) of the main part of the paper. Again, the main difference appears in the position of the O-2p bands.

The same layer by layer analysis of the projected DOS, as the one performed using GGA,

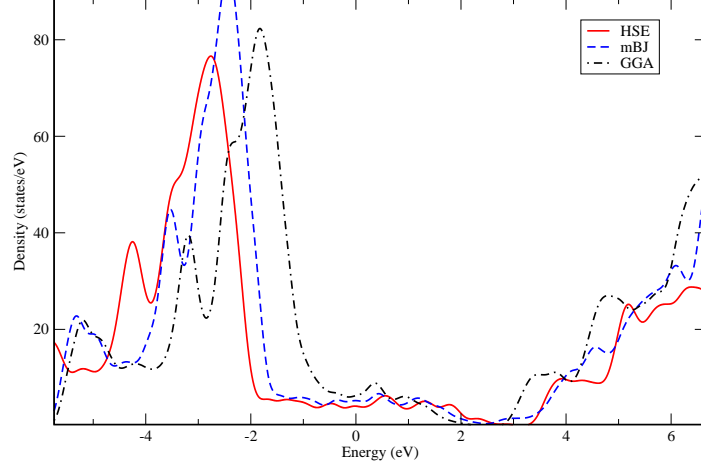


FIG. S2: (Color online) Total DOS for the 9 layer Bi- terminated BaBiO₃ (001) slab obtained with GGA, mBJ and HSE.

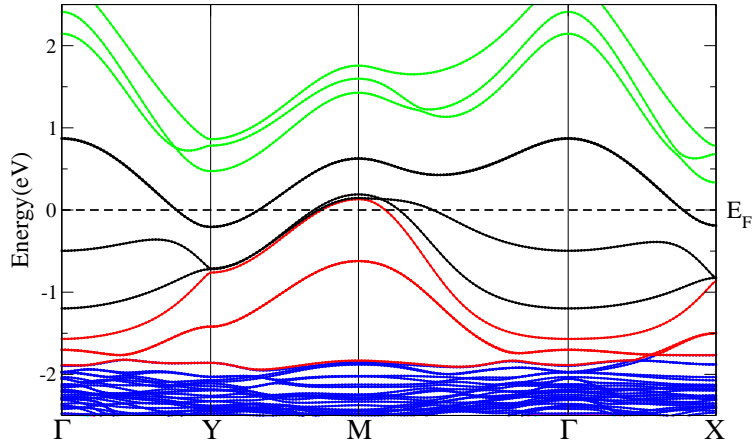


FIG. S3: (Color online) Bandstructure of the 9 layer Bi-terminated BaBiO₃ (001) slab. The color coding is the same as in Fig. 1 in the main part of the paper.

applies for mBJ and HSE. The three calculations show that the metallic states are confined to the outer planes of the slab.

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- [1] C. Franchini *et al.*, Phys. Rev. Lett. **102**, 256402 (2009).
 - [2] C. Franchini *et al.*, Phys. Rev. B **81**, 085213 (2010).
 - [3] H. J., S. G. E., and E. M., J. Chem. Phys. **118**, 8207 (2003).
 - [4] A. V. Krukau *et al.*, J. Chem. Phys. **125**, 224106 (2006).

- [5] F. Tran and P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009).
- [6] G. Kresse and J. Furthmüller, Comput. Matr. Sci. **6**, 15 (1996).
- [7] J. Paier *et al.*, J. Chem. Phys. **122**, 234102 (2005).
- [8] P. Blaha *et al.*, *WIEN2k, An augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Techn. Univ. Wien, Austria, SBN 3-9501031-1-2., 2002).
- [9] Y. Jeon *et al.*, Phys. Rev. B **41**, 4066 (1990).
- [10] M. Qvarford *et al.*, Phys. Rev. B **54**, 6700 (1996).